

SHORT COMMUNICATIONS

Preparation of Highly Heterotactic Polymethacrylate with Narrow Molecular Weight Distribution by *t*-Butyllithium/Bis(2,6-di-*t*-butylphenoxy)methylaluminum in Toluene

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Heterotactic polymer is a polymer which comprises an alternating sequence of meso and racemo diads. It is obvious that the formation of heterotactic polymer requires higher order of stereoregulation than those for isotactic and syndiotactic polymers, for which the control of configurational relationship between neighboring constitutional repeating units is sufficient in principle. In fact there have been few report on the formation of highly heterotactic polymer.¹ Only one exception is a heterotactic alternating copolymer of methyl methacrylate (MMA) and styrene prepared by a radical polymerization at -95°C in the presence of BCl_3 , the coheterotactic content being 89%.² The high alternating tendency of monomer sequence is essential for this high coheterotacticity. The highest heterotacticity so far reported for homopolymer is that for poly-(triisopropylsilyl vinyl ether) prepared with $\text{C}_2\text{H}_5\text{AlCl}_2$ in toluene at -78°C ($mm:mr:rr = 26:69:5$).³ Polymerization of methacrylates with octylpotassium in tetrahydrofuran (THF) gives heterotactic-rich polymers and the heterotacticity depends on the ester group

($mr = 51-65\%$) and is the highest for the benzyl ester (65%).⁴ Some α -phenylacrylate derivatives also give heterotactic-rich polymers^{4,5}; polymerization of methyl α -(*p*-chlorophenyl)acrylate in THF with butyllithium gives a polymer with mr of 67%.⁴ Formation of heterotactic polyacetaldehyde was also reported in the literatures.^{6,7}

We have reported stereospecific living polymerizations of MMA with $t\text{-C}_4\text{H}_9\text{MgBr}$ ^{8,9} and $t\text{-C}_4\text{H}_9\text{Li}$ /trialkylaluminum,^{10,11} which give highly isotactic and syndiotactic PMMAs, respectively, with narrow molecular weight distribution (MWD). Aluminum phenoxides bearing bulky substituents have been widely used in organic chemistry^{12,13} and recently in polymer chemistry.¹⁴⁻¹⁹ However, their use in stereospecificity control of the polymerization had not been reported, while chiral aluminum alkoxides have been used for asymmetric-selective polymerization of α -methylbenzyl methacrylate.¹⁹ Ballard *et al.*¹⁷ found that an initiator system comprising $t\text{-C}_4\text{H}_9\text{Li}$ and (2,6-di-*t*-butylphenoxy)diisobutylaluminum gave predominantly syndiotactic PMMAs with nar-

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row MWD in a living manner even at ambient temperature. We recently reported that a combination of $t\text{-C}_4\text{H}_9\text{Li}$ and bis(2,6-di-*t*-butylphenoxy)methylaluminum [$\text{MeAl}(\text{ODBP})_2$] gave heterotactic-rich PMMA with narrow MWD ($mr = 68\%$, $\bar{M}_w/\bar{M}_n = 1.06\text{--}1.17$) in the polymerization in toluene at -78°C .²⁰ In this work, we applied this initiator system to the polymerization of other alkyl methacrylates, and found that the primary and secondary esters gave heterotactic polymers with narrow MWD, among which ethyl (EMA) and butyl methacrylates gave polymers with the highest heterotactic triad content of 87%, which is the highest ever reported for homopolymer.

Methacrylate monomers were purified by fractional distillation, dried over calcium dihydride, and vacuum-distilled just before use. Toluene was purified in the usual manner, mixed with $n\text{-C}_4\text{H}_9\text{Li}$, and then distilled under high vacuum. $t\text{-C}_4\text{H}_9\text{Li}$ in pentane, obtained commercially, was used as a heptane solution. The concentration was determined by titration with butan-2-ol (1.20M).²¹ Bis(2,6-di-*t*-butylphenoxy)methylaluminum was prepared from 2,6-di-*t*-butylphenol and Me_3Al in toluene at room temperature and used for polymerization without further purification.

Polymerization was carried out in a glass ampoule filled with nitrogen passed through Molecular Sieves 4A cooled at -78°C .

$t\text{-C}_4\text{H}_9\text{Li}$ was added to a toluene solution of $\text{MeAl}(\text{ODBP})_2$ at polymerization temperature. The polymerization reaction was initiated by adding the monomer slowly to this mixture and terminated by adding methanol containing conc. HCl at the polymerization temperature. The solvent was removed under high vacuum, and the residue was dissolved in benzene. After insoluble materials were removed by centrifugation, the polymer was recovered from the solution by freeze-drying and dried under vacuum.

Tacticities of the polymers were determined from ^{13}C NMR spectra measured in nitrobenzene- d_5 at 110°C on a JEOL JNM-GSX270 spectrometer at 67.5 MHz. Molecular weight of the polymers and its distribution were determined by gel permeation chromatography (GPC) using a JASCO TRI ROTAR-V GPC chromatograph equipped with Shodex GPC columns KF-80M (30 cm \times 0.8 cm) and KF-802.5 (30 cm \times 0.8 cm) using chloroform as an eluent. The GPC chromatogram was calibrated against standard polystyrene samples.

Several alkyl methacrylates, all of which give isotactic polymers by the polymerization with $t\text{-C}_4\text{H}_9\text{Li}$ in toluene at -78°C ,^{11,22} were polymerized in toluene at -78°C with $t\text{-C}_4\text{H}_9\text{Li}/\text{MeAl}(\text{ODBP})_2$ (1/5). The results are shown in Table I. In all the cases, except for *t*-butyl methacrylate (*t*-BuMA), heterotactic

Table I. Polymerization of alkyl methacrylates with $t\text{-C}_4\text{H}_9\text{Li}/\text{bis}(2,6\text{-di-}t\text{-butylphenoxy})\text{methylaluminum}$ [$\text{MeAl}(\text{ODBP})_2$] (1/5) in toluene at -78°C for 24 h^a

Ester group	Yield %	\bar{M}_n (GPC)	\bar{M}_w \bar{M}_n	Tacticity/% ^b		
				<i>mm</i>	<i>mr</i>	<i>rr</i>
$-\text{CH}_3$	100	11640	1.14	11.6	67.8	20.6
$-\text{CH}_2\text{CH}_3$	100	7010	1.08	7.6	87.2	5.2
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	97.5	9300	1.07	8.4	87.1	4.5
$-\text{CH}_2\text{CH}(\text{CH}_3)_2$	84.3	6350	1.07	12.1	78.4	9.5
$-\text{CH}(\text{CH}_3)_2$	49.9	4730	1.07	2.1	69.2	28.7
$-\text{C}(\text{CH}_3)_3^c$	19.4	3050	1.19	7.4	8.5	84.1

^a Monomer 10 mmol; $t\text{-C}_4\text{H}_9\text{Li}$, 0.2 mmol; toluene, 10 ml.

^b Determined from ^{13}C NMR signals due to the main-chain quaternary carbon.

^c Polymerization time 48 h.

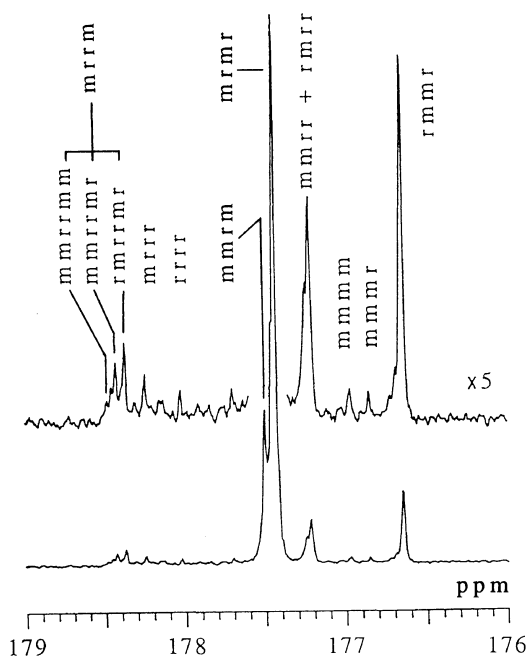


Figure 1. 67.5 MHz ^{13}C NMR spectrum of heterotactic poly(ethyl methacrylate) prepared with $t\text{-C}_4\text{H}_9\text{Li}/\text{bis}(2,6\text{-di-}t\text{-butylphenoxy})\text{methylaluminum}$ (1/5) in toluene at -78°C , measured in nitrobenzene- d_5 at 110°C .

polymethacrylates with narrow MWD's were obtained. The heterotacticity strongly depends on the structure of ester group and increased in the following order: t -butyl \ll methyl $<$ isopropyl $<$ isobutyl $<$ butyl \approx ethyl.

Except for the methyl ester, the linear alkyl esters were found to give higher heterotacticity and the highest heterotacticity of 87.2% was attained for poly(EMA). The assignments shown in the figure were made by the analogy from those for PMMA²³ and by the comparison with the spectrum of radically prepared poly(EMA). Figure 1 shows the carbonyl carbon region of the ^{13}C NMR spectrum of the heterotactic poly(EMA). The spectrum consisted of a strong $mmrm$ peak along with $mmrm$, $rmrr$, mmr , and $mrrm$ peaks as minor components. The signals due to other se-

Table II. Polymerization of ethyl methacrylate (EMA) with $t\text{-C}_4\text{H}_9\text{Li}/\text{bis}(2,6\text{-di-}t\text{-butylphenoxy})\text{methylaluminum}$ [$\text{MeAl}(\text{ODBP})_2$] (1/5) in toluene at -78°C for 24 h^a

Al	Yield	\bar{M}_n	\bar{M}_w	Tacticity/% ^b		
Li	%	(GPC)	\bar{M}_n	<i>mm</i>	<i>mr</i>	<i>rr</i>
1	25	2270	1.97	10.4	21.7	67.9
2	100	8360	1.08	7.2	82.1	10.7
3	100	7620	1.08	7.2	86.0	6.8
5	100	7010	1.08	7.6	87.2	5.2
7	100	6760	1.08	7.9	85.6	6.5
10	100	6370	1.08	7.8	85.2	7.0

^a EMA, 10 mmol; $t\text{-C}_4\text{H}_9\text{Li}$ 0.2 mmol; toluene, 10 ml.

^b Determined from ^{13}C NMR signals due to the main-chain quaternary carbon.

quences ($mrrr$, $rrrr$, $mmrr$ ^{*1}, $mmmm$, and $mmmm$) are scarcely observed. The results mean that the stereochemical defects in this heterotactic polymer are mainly mm and rr triads isolated in the heterotactic sequence; $\text{---}mmrm\text{---}$ and $\text{---}rmmr\text{---}$, the former being two times abundant as the latter. The other heterotactic polymers of primary esters, except for the PMMA, also showed larger mm content than rr content.

The rr content of the polymers increased as the bulkiness of ester group became larger, and the heterotactic poly(isopropyl methacrylate), a secondary ester, had an rr content larger than mm content. Further increase in bulkiness of the ester group gave rise to the predominant formation of rr sequence; t -BuMA gave a syndiotactic polymer with fairly narrow MWD in low yield, whose syndiotactic triad content (84%) was higher than those reported previously for the polymers prepared with $t\text{-C}_4\text{H}_9\text{Li}/(\text{C}_2\text{H}_5)_3\text{Al}$ (1/3) ($\bar{M}_w/\bar{M}_n = 1.64$, $mm:mr:rr = 10:33:57$)¹¹ and with $(\text{C}_6\text{H}_5)_3\text{P}/(\text{C}_2\text{H}_5)_3\text{Al}$ (1/2) ($\bar{M}_w/\bar{M}_n = 1.16$, $mm:mr:rr = 6:57:37$)²⁴. The decrease in polymer yield with increasing bulkiness of the ester group

*1 Although the $mmrr$ peak overlapped with the $rmrr$ peak, the contribution of the $mmrr$ peak could be estimated to be very small from the necessary relationship among pentad fractions²⁵; $(mmrr) = (mmmm) + 2(rmmr) - (mrrm) = 1.7\%$.

Table III. Polymerization of ethyl methacrylate (EMA) with *t*-C₄H₉Li/bis(2,6-di-*t*-butylphenoxy)-methylaluminum [MeAl(ODBP)₂] (1/5) in toluene at various temperatures^a

Temp °C	Time h	Yield %	\bar{M}_n (GPC)	\bar{M}_w \bar{M}_n	Tacticity/% ^b		
					<i>mm</i>	<i>mr</i>	<i>rr</i>
-95c	48	100	6810	1.08	8.4	87.6	4.0
-78	24	100	7010	1.08	7.4	87.3	5.3
-60	5	100	7240	1.19	1.2	23.4	75.4
-40	5	100	7580	1.44	0.5	15.0	84.5
-20	5	100	7690	1.54	1.1	21.6	77.3
0	5	100	7730	1.59	2.0	30.0	68.0
30	5	100	10840	1.73	2.8	32.7	64.5

^a EMA 10 mmol; *t*-C₄H₉Li 0.2 mmol; Al/Li=5; toluene 10 ml. *t*-C₄H₉Li and MeAl(ODBP)₂ were mixed at -78°C, regardless of polymerization temperature.

^b Determined from ¹³C NMR signals due to the main-chain quaternary carbon.

^c Toluene 5 ml.

suggests the importance of activation of the monomers through coordination by MeAl(ODBP)₂.^{14,15,17}

Table II shows the effect of the ratio of MeAl(ODBP)₂ to *t*-C₄H₉Li for the polymerization of EMA with *t*-C₄H₉Li/MeAl(ODBP)₂. At the Al/Li ratio of 1, a predominantly syndiotactic polymer was obtained. Highly heterotactic poly(EMA)s with narrow MWD were obtained at the Al/Li ratios of 2 to 10. The heterotacticity reached a maximum at the Al/Li ratio of 5 as in the case of the polymerization of MMA.²⁰ The \bar{M}_n of the poly(EMA) decreased with increasing Al/Li ratio. This means that the initiator efficiency increased as the Al/Li ratio increased, probably because the aluminum phenoxide promotes dissociation of *t*-C₄H₉Li aggregated in toluene. A similar effect of aluminum compounds has been discussed for the polymerization with *t*-C₄H₉Li/R₃Al.¹¹

Table III shows the effects of temperature on the polymerization of EMA with *t*-C₄H₉Li/MeAl(ODBP)₂ in toluene at the Al/Li ratio of 5. The tacticity of poly(EMA) was quite sensitive to the polymerization temperature, as in the case of the polymerization of MMA under the same conditions,²⁰ and changed drastically from heterotactic to syndiotactic

with increasing temperature. In the temperature range from -60°C to 30°C, predominantly syndiotactic poly(EMA)s were formed. The syndiotacticity was the highest at -40°C (*rr*=84.5%). The initiator efficiency decreased with increasing temperature while the MWD became broad.

Provided that the aluminum phenoxide coordinates the polymer anion in 1:1 ratio, the fact that the syndiotactic polymer formed at Al/Li=1 in low yield at -78°C (Table II) suggests that the coordinated polymer anion is less reactive and polymerizes non-activated free monomer in a syndiotactic-specific way. When the excess phenoxide exists (Al/Li ratio > 1), it coordinates with EMA to activate the monomer and the propagation might occur mainly with the activated monomer, which is heterotactic-specific. This assumption is consistent with the decrease of polymer yields with increasing bulkiness of the monomer (Table I). At higher temperature, however, the coordinated polymer anion becomes active enough to add the non-activated monomer, giving the syndiotactic polymer.

¹H NMR analysis of the polymer revealed that the polymer contains one *t*-butyl group at the chain end (0.856 ppm in nitrobenzene-*d*₅ at 110°C), indicating that *t*-C₄H₉Li initiates the

polymerization. The \bar{M}_n , determined from the end-group analysis by ^1H NMR spectroscopy, increased proportionally to polymer yield, while the amount in mmol of polymer molecules was independent of the yield, the value of which corresponded to 77% of $t\text{-C}_4\text{H}_9\text{Li}$ used at $\text{Al/Li}=5$. These results, as well as the narrow MWD's of the polymers obtained, indicate that the polymerization has the living character, although the initiator efficiency was less than unity. Further details of the living polymerization will be published in the near future.

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